

THE PREPARATION OF SILICA AEROGELS FROM
METHYL ORTHOSILICATE IN AN ALCOHOLIC
MEDIUM AND THEIR PROPERTIES

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16. Abstract A silica aerogel is prepared by hydrolysis in an autoclave of methyl orthosilicate in methanolic solution. The alcohol is removed when its critical temperature has been exceeded slightly. An advantage of this method over the usual method of preparing aerogels in an initially aqueous medium is that it does not require a change of solvent before the autoclave treatment and requires no handling of the gel while it is still impregnated with alcohol and is thus mechanically fragile. Extremely high-porosity silica aerogels (porous volume on the order of 18 cm ³ /g) have been obtained by this method.			
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Introduction

/1906*

The method usually used to dry a precipitated gel still impregnated with solvent is to evaporate the solvent either in a vacuum or by heating with air. The evaporation produces a liquid-gas interphase within the pores which exerts considerable stresses on the gel due to the surface tension of the liquid. The texture of the resultant dry solid is quite different from that of the gel saturated with solvent, due to the collapse of the initial texture produced by this surface tension. The only way of preventing this change in the porous texture is to eliminate the liquid-gas interphase. Kistler [1] prepared the first of these solids, which are called "aerogels," by heating the gel in an autoclave until the critical temperature of the solvent was reached. Under these conditions, the liquid was converted into gas continuously without the two phases being simultaneously present in the pores at any time. The texture of a solid of this type, therefore, has not been subjected to any surface tension. Furthermore, Kistler [1] found that in the vicinity of the critical conditions, water becomes a dissolving agent which is so powerful that some mineral compounds such as silica are peptized during heating in an autoclave with pressurized steam. Thus the dry solid obtained is not very porous. This problem may be prevented by replacing the water with which the gel is initially impregnated by an organic solvent prior to evaporation in the autoclave.

* Numbers in the margin indicate pagination in the foreign text.

For these reasons, the method usually used to prepare silica aerogels is to precipitate a hydrogel, by acidification of an aqueous sodium silicate solution, for example. This hydrogel is then fragmented and washed with distilled water until the sodium chloride which is formed simultaneously has been completely removed. The water is then replaced with an organic solvent such as alcohol and the gel, impregnated with this solvent, is dried under hypercritical conditions in an autoclave. We have recently described a similar method of preparing silica aerogels [2].

To eliminate these various handling operations, which are harmful to the texture of the gel, we have developed a method for preparing silica aerogels which requires a minimum of operations such as washing, fragmentation of the gel, decanting of the gel, and replacement of the water with an organic liquid. This method involves the use of a methanol-soluble silicon derivative; the methanol is directly used as the precipitation medium in place of water so that it is not necessary to change the solvent prior to the autoclave treatment. The washing operation is eliminated by the use of chemical reactants which furnish byproducts to the reaction which are all volatile under the autoclave conditions.

The hydrolysis of silicon tetrachloride or a silicon alcoholate in an alcohol solution fulfills the above conditions. However, since the hydrolysis of silicon tetrachloride generates large quantities of hydrochloric acid, it is necessary to use an autoclave resistant to the corrosion provoked by this acid at high temperatures (approximately 260° C). For this reason, methyl orthosilicate, which does not yield any corrosive byproducts, was chosen as an initial reactant.

Experimental Techniques

Preparation of Silica Aerogels by Hydrolysis of Methyl Orthosilicate

The quantity of water necessary for hydrolysis, ranging from 2 to 20 molecules per silica molecule, is added at 0° C to methyl orthosilicate dissolved in methanol at a concentration of 5 to 30% by volume. The solution obtained may be acidified by acetic acid or alkalyzed by ammonia, depending on whether the intention is to obtain precipitation in an acidic or a basic medium. 5 cm³ of this solution are poured into a test tube placed in an autoclave with a volume of 300 cm³. An adequate quantity of alcohol (95cm³) so that the critical pressure will be exceeded at the end of the temperature increase is also poured into the autoclave. The autoclave is immediately closed and heated to 260° C in 2 1/2 hours. The temperature increase is made as linear as possible, at a rate of 1.6° C per minute. /1907

The polycondensation of silicic acid generated by hydrolysis, which results in gelation, occurs during the increase in temperature of the autoclave. The alcohol is evaporated when its critical temperature has been exceeded slightly. The dry aerogel is removed from the autoclave when the latter has been returned to the ambient temperature under a current of dry nitrogen.

This method offers the following advantages over the usual methods for preparing aerogels.

1. Since methyl orthosilicate is soluble in methanol, the silica gel is precipitated directly in an alcoholic medium. As a result, it is unnecessary to change the solvent before drying in the autoclave.
2. The use of a silicon reactant results in products which are all volatile under the autoclave conditions (with the

exception of silica), making it possible to eliminate washing of the gel. All these byproducts are eliminated in gaseous form.

3. As a result of the above two advantages, preparation by this method is much simpler and faster than any described so far, since the operations of washing and changing the solvent are always lengthy and laborious and tend to damage the texture of the gel.

Methods of Analysis of the Solids Obtained

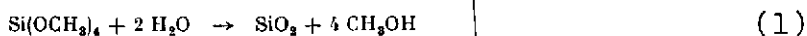
The methods and techniques used to analyze the texture of the solids obtained has been described previously [2,3].

Experimental Results and Discussion

Textural Properties of the Aerogels Obtained by Hydrolysis of Methyl Orthosilicate

1. Effect of the Quantity of Water

The overall precipitation reaction of silica is represented by the equation:



Actually, the compound which is precipitated is a more or less polycondensed polysilicic acid. Consequently the aerogel obtained is not represented by the formula SiO_2 , but rather by the formula $\text{SiO}_2, n \text{H}_2\text{O}$, with $n \leq 2$; n is equal to 2 in cases where the reaction is limited to the formation of monomer silicic acid according to the equation:

(2)

It appeared that the precipitation was quite incomplete in an acidic medium (0.175 N acetic acid) when the quantity of water used was rigorously stoichiometric (equation 1). The porosity of the aerogel obtained under these conditions by the hydrolysis of a 10% solution of methyl orthosilicate in methanol (gel E_1) is extremely low in comparison to that of all the aerogels obtained with excess water. When a quantity of water equal to twice the stoichiometry of Reaction 1 is used, the aerogel obtained (E_2) occupies the entire volume of the alcoholic methyl orthosilicate solution initially placed in the autoclave and has considerably improved textural characteristics. It has thus been possible to prepare aerogels whose total macroporosity (V_p) is close to $18 \text{ cm}^3/\text{g}$ (E_3). When the water concentration becomes too high (gel E_4) the macroporosity decreases considerably (Table 1).

TABLE 1

Aerogel	$\frac{\text{H}_2\text{O}}{\text{Si}(\text{OCH}_3)_4}$	p (mg)	V_p (cm^3/g)	S_{As} (m^2/g)	S_{Al} (m^2/g)	V_{pA} (cm^3/g)	S_N (m^2/g)	V_{pN} (cm^3/g)
E_1	2	118	2.7	373	386	0.15	380	0.18
E_2	4	240	11.6	776	780	0.72	865	1.82
E_3	10	285	17.3	627	650	0.62	688	1.72
E_4	20	213	7.2	384	410	0.40	405	1.52

- p : Weight of aerogel obtained by hydrolysis of 0.5 cm^3 methyl orthosilicate.
- V_p : Macroporous volume, determined by the introduction of mercury (diameter of pores $> 580 \text{ \AA}$).
- S_{As} : Specific area, determined by adsorption of argon with $(p_0)_s$ the vapor tension of solid argon ($\sigma_{AS} = 16.2 \text{ \AA}^2$, the cross section of the argon atom in the adsorbed state, calculated with $[p_0]_s$).
- S_{Al} : Specific area, determined by adsorption of argon with $(p_0)_l$ the vapor tension of liquid argon ($\sigma_{Al} = 15.5 \text{ \AA}^2$, the cross section of an argon atom in the adsorbed state, calculated with $[p_0]_l$).
- V_{pA} : Microporous volume, measured with argon (diameter of pores $< 200 \text{ \AA}$).
- S_N : Specific area, determined by adsorption.
- V_{pN} : Porous volume, determined by adsorption of nitrogen (diameter of pores $< 840 \text{ \AA}$).

All the textural properties of the aerogels obtained by this method reach a maximum with a given quantity of water ranging from 2 to 5 times the stoichiometric quantity (Reaction 1). The adsorption-desorption isotherms of argon and nitrogen by gels E_1 , E_2 and E_4 (for the sake of clarity, the isotherms for gel E_3 , which were very close to those of gel E_2 , have not been plotted), shown in Figs. 1 and 2, indicate that the solid E_1 , prepared with the stoichiometric quantity of water, has a low adsorption capacity even though it is extremely microporous (type I isotherm according to the Brunauer classification [4]). Aerogels precipitated by silica molecules in the presence of 4 molecules of water or more have type II argon and nitrogen adsorption isotherms (Figs. 1 and 2).

Roughly similar developments are observed in a neutral medium. The porosity accessible to gases in the adsorbed state (V_{pA} and V_{pN}) increases as the quantity of water introduced changes from 2 to 4 H_2O per $Si(OCH_3)_4$ and subsequently undergoes little variation. The volume of the macropores, V_p , also is no longer affected by a large excess of water (Table 2). The decrease in specific area is probably due to the partial dissolution of the silica by the excess pressurized water. An identical phenomenon has been observed in the case of aerogels precipitated in an aqueous medium in which the water has been replaced with methanol by washing with a Soxhlet apparatus [2]. In this case, too large a quantity of residual water (on the order of 1%) resulted in dissolution of the silica in the autoclave followed by the reprecipitation of a partially crystallized and therefore less porous solid. /1908

In a 0.5 N ammonia medium, precipitation is much more complete than in a neutral or acidic medium, even with the stoichiometric quantity of water (Reaction 1), as shown by the weights of the gel obtained (Table 3). However, in an alkaline medium, silica

sol is much less stable, and when the water concentration is more than twice the stoichiometry of Reaction 1, there is partial precipitation of silica alkogel as soon as it is introduced into the hydrated and alkalized methanol in methyl orthosilicate. For this reason, the effects of water concentration in an alkaline medium cannot be analyzed with quantities more than twice the stoichiometric quantity.

The aerogels obtained in an alkaline medium have a much more developed macroporosity (V_p) than that of solids precipitated in a neutral or acidic medium, even though their macroporosities (V_{pN} and V_{pA}) are comparable.

TABLE 2

Aerogel	$\frac{H_2O}{Si(OCH_3)_4}$	p (mg)	V_p (cm ³ /g)	S_{AB} (m ² /g)	S_{AI} (m ² /g)	V_{pA} (cm ³ /g)	S_N (m ² /g)	V_{pN} (cm ³ /g)
E_5	2	110	7.9	347	346	0.23	366	0.40
E_6	4	193	10.7	752	742	0.71	746	1.53
E_7	10	213	15.4	544	526	0.53	590	1.58
E_8	20	210	16.3	493	492	0.54	523	1.48

TABLE 3

Aerogel	$\frac{H_2O}{Si(OCH_3)_4}$	p (mg)	V_p (cm ³ /g)	S_{AB} (m ² /g)	S_{AI} (m ² /g)	V_{pA} (cm ³ /g)	S_N (m ² /g)	V_{pN} (cm ³ /g)
E_9	2	197	4.6	719	743	0.61	820	1.64
E_{10}	4	225	5.3	615	600	0.51	697	2.06

2. Effect of Methyl Orthosilicate Concentration

The effect of the methyl orthosilicate concentration was studied in a slightly acidic medium (0.175 N acetic acid) in the presence of twice the stoichiometric quantity of water (4 molecules water per silica molecule).

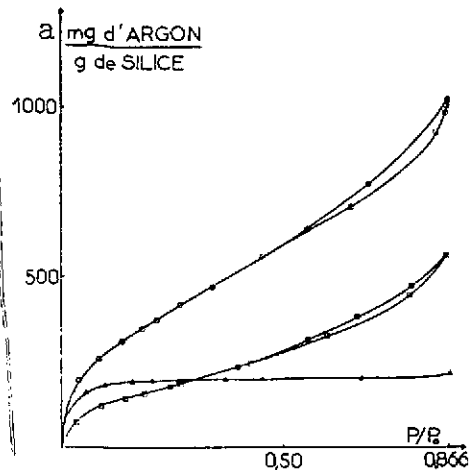


Fig. 1. Isotherms for the adsorption and desorption of argon by aerogels E₁ (Δ), E₂ (O) and E₄ (□).

Key. a. $\frac{\text{mg argon}}{\text{g silica}}$

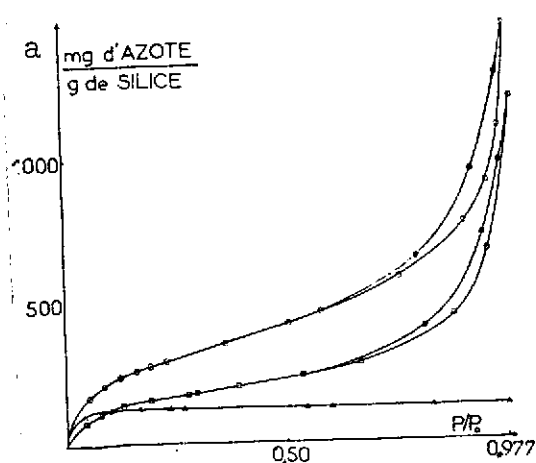


Fig. 2. Isotherms for the adsorption and desorption of nitrogen by aerogels E₁ (Δ), E₂ (O) and E₄ (□).

Key. a. $\frac{\text{mg nitrogen}}{\text{g silica}}$

The results, given in Table 4, show that aerogel E₁₁, prepared from a solution of 5% methyl orthosilicate by volume in methanol has much lower microporosity and macroporosity than that of other solids (Table 4).

At the same time, the quantity of aerogel removed from the autoclave is much lower than that of the initial solution of methyl orthosilicate in methanol. However, as soon as the reactant concentration is 10%, the aerogel formed occupies a volume quite close to that of the initial solution, and its apparent density d_a is consequently closely proportional to the initial methyl orthosilicate concentration, as indicated by the experimental values given in Table 4. Thus it is normal that the porous volumes, measured by gas adsorption and especially by mercury penetration, decrease as the methyl orthosilicate solution increases from 10 to 30%, since the apparent density of the aerogels increases. On the other hand, the initial methyl orthosilicate concentration has very little influence on the specific

/1909

area in the 10 to 30% range (Table 4). Figures 3 and 4, showing the adsorption-desorption isotherms of argon and nitrogen by gels E_2 , E_{11} and E_{13} show that aerogel E_{11} , prepared from the most dilute solution (5%) of methyl orthosilicate, is an essentially microporous solid since its isotherms are type I according to the Brunauer classification [4].

TABLE 4

Aerogel	$[\text{Si}(\text{OCH}_3)_4]$ (% by volume)	p (mg)	d_a (g/cm ³)	V_p (cm ³ /g)	S_{As} (m ² /g)	S_{Al} (m ² /g)	V_{pA} (cm ³ /g)	S_N (m ² /g)	V_{pN} (cm ³ /g)
E_{11}	5	103	0.27	1.2	596	592	0.23	524	0.21
E_2	10	240	0.04	11.6	776	780	0.72	865	1.82
E_{12}	20	491	0.10	10.0	749	771	0.68	805	1.55
E_{13}	30	724	0.16	4.0	815	821	0.60	774	1.46

d_a : apparent density of solid

TABLE 5

Aerogel	$[\text{CH}_3\text{COOH}]$ (moles/liter)	V_p (cm ³ /g)	S_{As} (m ² /g)	S_{Al} (m ² /g)	V_{pA} (cm ³ /g)	S_N (m ² /g)	V_{pN} (cm ³ /g)
E_5	0.000	10.7	752	742	0.71	796	1.53
E_{14}	0.060	10.0	780	798	0.71	875	1.89
E_2	0.175	11.6	776	780	0.72	865	1.82
E_8	0.350	11.4	790	785	0.73	839	1.82
E_{15}	0.700	12.0	764	749	0.69	815	1.56
E_{17}	1.050	12.3	719	739	0.70	789	1.56

3. Effect of Acid Concentration

The effect of the acid concentration was studied by adding increasing quantities of acetic acid to a 10% solution of methyl orthosilicate in methanol. The results show that the porosity of solids precipitated in the presence of 4 molecules water per molecule of methyl orthosilicate is not very sensitive to acid concentration (Table 5).

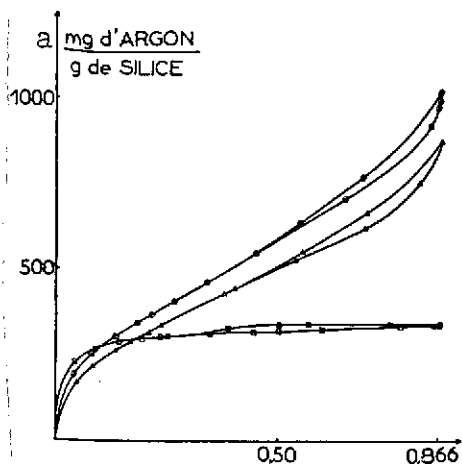


Fig. 3. Adsorption-desorption isotherms of argon by aerogels E₂ (O), E₁₁ (□) and E₁₃ (Δ).

Key. a. $\frac{\text{mg argon}}{\text{g silica}}$

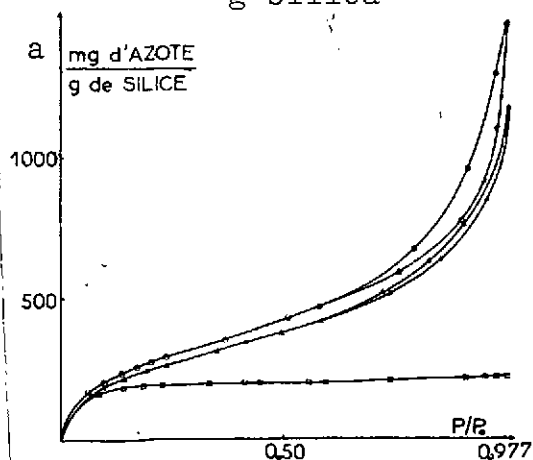


Fig. 4. Adsorption-desorption isotherms of nitrogen by aerogels E₂ (O), E₁₁ (□) and E₁₃ (Δ).

Key. a. $\frac{\text{mg nitrogen}}{\text{g silica}}$

The specific area and the porous volumes V_p and V_{pA} underwent little variation as the acetic acid concentration in the solution increased from 0 to 1 mole per liter. Only the porous volume measured with nitrogen V_{pN} increased slightly as the medium became more acidic, and then decreased appreciably once the acetic acid concentration became higher than 0.35 moles per liter.

4. Effect of Ammonia Concentration

Similar tests were performed on an alkaline medium by adding to a 10% by volume solution of methyl orthosilicate in methanol an aqueous ammonia solution whose concentration was such that the ratio $\text{H}_2\text{O}/\text{Si}(\text{OCH}_3)_4$ always remained equal to 4.

It thus appears that the textural characteristics (specific area, V_{pA} and V_p) decrease as the alkalinity of the solution increases, with the exception of the porous volume measured with nitrogen, which reaches a maximum with an ammonia concentration of close to 0.2 moles per liter (Table 6).

This decrease in textural characteristics seems to be a completely generalized phenomenon: no matter what method is used /1910 to obtain the gel, the solids obtained in an alkaline medium always have a lower specific area and a lower micropore volume than those of gels precipitated in an acidic or neutral medium. We have already pointed out this phenomenon in the case of gels prepared by the hydrolysis of silicon tetrachloride in methanol [2] and by the acidification of an aqueous sodium metasilicate solution [5].

Thermal Stability of Aerogels

The thermal stability of the aerogels prepared was studied in a high temperature range ($\approx 1000^\circ \text{C}$). For this purpose, an aerogel (E_{20}) precipitated by hydrolysis of a 10% methyl orthosilicate solution in the presence of 0.175 N acetic acid and a quantity of water twice the stoichiometry of Reaction 1 was subjected to heat treatment in air for 8 hours at temperatures ranging from 300 to 900°C .

The results given in Table 7 show that heating to 500°C notably improves the macroporosity of the aerogels ($16.5 \text{ cm}^3/\text{g}$ in place of $11.1 \text{ cm}^3/\text{g}$). The porous volume accessible to mercury is much lower than that of the initial solid only with treatment temperatures of more than 700°C . On the other hand, the porosity accessible to gases in the adsorbed state (V_{pN} and V_{pA}) decreases regularly as the temperature increases (Table 7).

The adsorption-desorption isotherms for argon (Fig. 5) and nitrogen (Fig. 6) show that the quantity of gas adsorbed at a given relative pressure decreases considerably when the temperature of the heat treatment is higher than 300°C .

TABLE 6

Aerogel	[NH ₄ OH] (moles/liter)	V _p (cm ³ /g)	S _{As} (m ² /g)	S _{Al} (m ² /g)	V _{ρ_A} (cm ³ /g)	S _n (m ² /g)	V _{ρ_n} (cm ³ /g)
E ₀	0.0	10.7	752	742	0.71	796	1.53
E ₁₈	0.2	5.9	644	673	0.59	704	2.44
E ₁₀	0.5	5.3	615	600	0.51	697	2.06
E ₁₉	1.0	6.9	489	503	0.46	530	1.50

TABLE 7

T (°C)	V _p (cm ³ /g)	S _{As} (m ² /g)	S _{Al} (m ² /g)	V _{ρ_A} (cm ³ /g)	S _n (m ² /g)	V _{ρ_n} (cm ³ /g)
—	11.1	824	821	0.71	860	1.81
300	13.1	858	870	0.70	1 004	1.48
500	16.5	724	704	0.56	800	1.26
700	10.5	435	437	0.37	477	0.90
900	6.5	145	141	0.14	162	0.30

T: temperature of heat treatment.

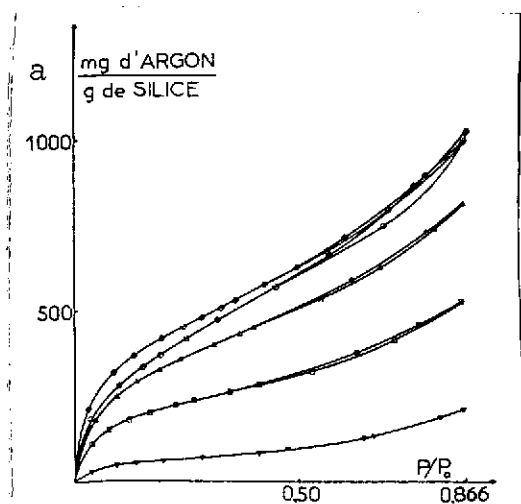


Fig. 5. Adsorption-desorption isotherms of argon by aerogel E₂₀ in its initial state (0) and heated for 8 hours in air at 300° C (◇), 500° C (Δ), 700° C (□) and 900° C (▽).
Key. a. $\frac{\text{mg argon}}{\text{g silica}}$

These tests showed that silica aerogels prepared by the hydrolysis of methyl orthosilicate have high heat stability up to 700° C in regard to their macroporous structure. Furthermore, /1911 neither the apparent density nor the appearance of the aerogels is appreciably changed as long as the heating temperature is no higher than 700° C.

Conclusions

The method for preparing silica aerogels which uses the hydrolysis of methyl orthosilicate

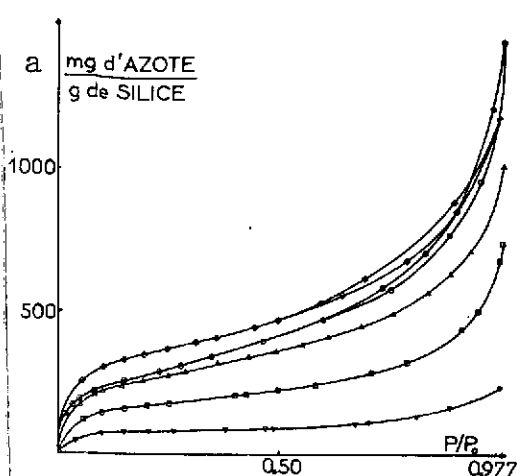


Fig. 6. Adsorption-desorption isotherms of nitrogen by aerogel E₂₀ in its initial state (O)²⁰ and heated in air for 8 hours to 300° C (◇), 500° C (Δ), 700° C (□) and 900° C (▽).

Key. a. $\frac{\text{mg nitrogen}}{\text{g silica}}$

white, opaque silica which assumes the shape of the tube containing it. Their specific area is close to 800 m²/g of the porous volumes measured by gas adsorption; on the order of 0.700 cm³/g (V_{PA}) and 1.50 cm³/g (V_{PN}), and a macroporous volume, determined by mercury penetration, which may be as high as 17.3 cm³/g.

The aerogels obtained in an alkaline medium are completely transparent, even at a thickness of 1 cm.

This research was performed with the financial aid of the Research and Test Methods Administration.

in an alcohol solution is a simple and fast process making it possible to obtain solids of extremely high porosity (12 to 18 cm³/g). To obtain properties of this sort, the solidification of the solution, which occurs during the temperature rise in the autoclave, must affect the entire volume of the solution. This condition is met if the methyl orthosilicate concentration in the methanol is greater than 5 to 10% of the solution by volume and if the quantity of water present in the medium is between 2 and 5 times the stoichiometric quantity of Reaction 1. The aerogels obtained under these conditions occur in the form of a single piece of

REFERENCES

1. Kistler, S. S., J. phys. Chem., 36, 52 (1932). S. S. Kistler, U.S. Patent 2093454, 2188007, 2249767.
2. Nicolaon, G.A. and S.J. Teichner, Bull. Soc. chim., 1968, p. 1900.
3. Nicolaon, G.A. and S.J. Teichner, J. Chim. phys., 1968, p. 870.
4. Brunauer, S., L.S. Demin, W.E. Deming and E. Teller, J. amer. chem. Soc., 62, 1723 (1940).
5. Nicolaon, G.A. and S.J. Teichner, Bull Soc. chim. (forthcoming).